

METHOD 41

REF: Regs:	8-3	8-14	8-29	8-45
	8-4	8-19	8-31	8-51
	8-11	8-20	8-32	
	8-12	8-23	8-38	
	8-13	8-26	8-43	

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOLVENT BASED COATINGS AND RELATED MATERIALS CONTAINING PARACHLOROBENZOTRIFLUORIDE

- 1.1 This method is applicable to the determination of parachlorobenzotrifluoride (**PCBTF**) in solvent based coatings and related products.
- 1.2 The concentration of parachlorobenzotrifluoride is determined by gas chromatography using ethanol, or any appropriate solvent, as the internal standard.
- 1.3 For multicomponent coating systems, the components must be mixed first in the appropriate ratio. The exempt solvents, density and total non-volatiles are determined from this mixture. The total non-volatile content is determined by allowing the test specimens to have an induction period of 30 minutes in the aluminum dish prior to oven heating.
- 1.4 Propylene glycol monomethyl ether acetate, interferes with the analysis of parachlorobenzotrifluoride. When this solvent is present in the sample, use the alternate column (2.2.2).
- 1.5 This method may not be applicable to all types of coatings or printing inks. ~~Other procedures may be substituted with mutual agreement of the manufacturer, user and the Air Pollution Control Officer (APCO).~~

2) APPARATUS

- 2.1 **Gas Chromatograph.** This unit is fitted with a flame ionization detector (FID), a glass sleeve injection port, a temperature programmer and a compatible integrator or data station. The suggested operating parameters are as follows:

Initial Oven Temperature (°C)	60
Initial Hold time (min)	5
Temperature Program Rate (°C/min)	5
Final Oven Temperature (°C)	200
Final Hold time (°C)	10
Injector Temperature (°C)	250

Detector Temperature (°C)	250
Carrier Gas	He
Carrier Gas Flow (cc/min)	20
Injection Sample Size (µl)	1

2.2 Analytical Column. Any column capable of separating and resolving the compounds of interest is acceptable. The suggested analytical columns for this method are:

2.2.1 Primary Column. A 12' x 1/8" O.D. SS column packed with 20% SP-2100/0.1% Carbowax 1500, 100/120 mesh Supelcoport. The packing material is available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048.

2.2.2 Alternate column for the analysis of parachlorobenzotrifluoride. A 60M x 0.32mm ID DB-WAX Column, 1.0 µm film thickness. This column is available from J & W Scientific, 91 Blue Ravine Road, Folsom, CA 95630-9928.

2.3 10 µl Syringe.

2.4 Burrell Wrist Action Shaker.

2.5 Desiccator.

2.6 Aluminum Foil Dish. 57 mm diameter x 10 mm high with a flat bottom.

2.7 Forced Draft Oven. Capable of maintaining a temperature of $110^{\circ} \pm 5^{\circ}\text{C}$.

2.8 Analytical Balance. Capable of weighing to ± 0.0001 g

2.9 Top Loading Analytical Balance. Capable of weighing to ± 0.01 g.

2.10 Disposable Beral Pipettes. These are available from Curtin Matheson Company (Catalog #376-970).

2.11 Spatula.

2.12 Gardner Weight Per Gallon Cup, 83 cc. This cup is available from Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085 (Catalog # 8353A01).

6.6 Vials with screw caps, 2 dram size.

2.14 Eberbach Shaker for quart or less size containers

2.15 Red Devil Paint Shaker for gallon size containers.

2.16 Disposable Syringe. 3-5 cc used for coatings with highly volatile solvents.

3) REAGENTS

- 3.1 Toluene or other suitable solvent, reagent grade.
- 3.2 Ethanol, Absolute, 200 proof or other suitable anhydrous solvent.
- 3.3 Dimethylformamide (DMF). Spectroquality. Water content must not exceed 0.05% (w/w). Other suitable solvents, Reagent grade.
- 3.4 Helium or Nitrogen, 99.995% or higher.
- 3.5 Hydrogen.
- 3.6 Air.
- 3.7 Parachlorobenzotrifluoride. Reagent grade or highest available quality.
- 3.8 Propylene Glycol Monomethyl Ether Acetate. Reagent grade.

4) ANALYTICAL PROCEDURE

4.1 Determination of Total Volatiles. (NOTE 1)

- 4.1.1 Mix the coating thoroughly for about 30 minutes, using an Eberbach or Red Devil Paint Shaker. It is essential that the samples be well mixed to obtain valid results. Stirring with a spatula after mixing is also required.
- 4.1.2 Precondition the aluminum dish (2.6) containing a paper clip in the oven for at least 30 minutes at $110^{\circ} \pm 5^{\circ}\text{C}$. Cool and store in a desiccator. Weigh accurately the aluminum dish with the paper clip to ± 0.0001 g.
- 4.1.3 Using a disposable Beral pipette, weigh accurately 0.4 to 0.6 g (± 0.0001 g) of the thoroughly mixed coating (4.1.1) in the pre-weighed aluminum dish containing a paper clip. Record the total weight of the sample and dish in grams.
- 4.1.4 Disperse the coating by adding 2 ml of toluene or any appropriate solvent and stir with the paper clip until the sample is evenly dispersed. Dry the sample in the oven at $110^{\circ} \pm 5^{\circ}\text{C}$ for 1 hour. Cool the sample in the desiccator and weigh.
- 4.1.5 Run the analysis in duplicate. Reanalyze the sample if results vary by more than $\pm 1\%$ (absolute) of the mean.

NOTE 1: For multicomponent systems, premix the components in the correct proportions. Weigh accurately 0.2 - 0.4 g (± 0.0001 g) of mixture into a tared aluminum dish with paper clip. Disperse the sample in the aluminum dish using the paper clip, without adding any solvent. Allow an induction period of 30 minutes, prior to oven drying. Use the same mixture for the determination of density and parachlorobenzotrifluoride.

4.2 Calculations for the Determination of Total Volatile and Non-Volatile Contents.

4.2.1 Weight of Coating = (4.1.3) - (4.1.2)

Where: (4.1.3) = Weight of the coating and aluminum pan (g)
(4.1.2) = Weight of the aluminum pan (g)

4.2.2 Weight of Non-Volatile (NV) = (4.1.4) - (4.1.2)

Where: (4.1.4) = Weight of the non-volatile and aluminum pan (g)

4.2.3 % NV (w/w) = $\frac{(4.2.2) \times 100}{(4.2.1)}$

6.6.1 % Total Volatiles in Coating = 100% - (4.2.3)

4.3 Determination of Density.

6.6.1 Calibrate the volume of the Gardner weight per gallon cup as described in ASTM D 1475-90.

4.3.2 Accurately weigh the cup **(4.3.1)** to ± 0.01 g.

4.3.3 Completely fill the cup with the thoroughly mixed coating **(4.1.1)**. Cap the container, leaving the overflow orifice open. Immediately remove excess overflow sample material by wiping dry with absorbent material. Avoid occluding air bubbles in the container.

4.3.4 Accurately weigh the filled cup to ± 0.01 g.

4.3.5 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than 0.006 g/ml.

6.6.1 Calculation of Density.

$$D \text{ (g/ml)} = \frac{(4.3.4) - (4.3.2)}{(4.3.1)}$$

Where: D = Density (g/ml).
(4.3.1) = Volume in ml of the calibrated cup
(4.3.4) = Weight of the cup filled with coating (g)
(4.3.2) = Weight of the cup (g)

4.4 Determination of Parachlorobenzotrifluoride Content of the Coating by Gas Chromatography.

4.4.1 Set up the gas chromatograph as described in **Section 2.1**.

4.4.2 Screen the sample for the presence of peaks interfering with the internal standard.

6.6.1.1 Prepare a solution of ethanol in DMF by weighing approximately 0.2 grams of ethanol into a vial containing 4 ml DMF. (NOTE 2).

NOTE 2: Dimethylformamide is harmful if inhaled or absorbed through the skin. It is suspected to be embryotoxic. Use only with adequate ventilation. Avoid contact with skin, eyes and clothing. If the material to be analyzed is not compatible with DMF, then use a different solvent such as Carbon Disulfide. If Carbon Disulfide is used, change the internal standard to isopropanol or any other appropriate compound. Ethanol is not completely miscible with CS₂.

4.4.2.2 Inject a 1 µl aliquot of the solution (**4.4.2.1**) into the gas chromatograph. Retain the chromatogram.

4.4.2.3 Weigh approximately 0.5 grams of the mixed sample into a vial containing 4 ml of DMF. Mix thoroughly and allow to stand for about 5 minutes. Inject a 1 µl aliquot of the mixture into the gas chromatograph. Compare the sample chromatogram to that obtained in **Section 4.4.2.2**. If there is no peak that interferes with ethanol in the sample chromatogram, then proceed to **Section 4.4.3**. If an interfering peak is found use 2-propanol or any other appropriate solvent as the internal standard.

6.6.2 Screen the sample for the presence of propylene glycol methyl ether acetate (PGMEA), (NOTE 3).

NOTE 3: It is necessary to screen the sample for PGMEA since this compound coelutes with PCBTF when using the primary column.

4.4.3.1 Prepare a Propylene glycol monomethyl ether acetate solution in DMF by weighing approximately 0.2 grams of propylene glycol monomethyl ether acetate into a vial containing 4 ml DMF.

4.4.3.2 Inject a 1 μ l aliquot of the solution (**4.4.3.1**) into a gas chromatograph fitted with the alternate column (**2.2.2**) (**NOTE 4**). Retain the chromatogram.

4.4.3.3 Inject a 1 μ l aliquot of the sample prepared in **Section 4.4.2.3** and compare the chromatogram with the one obtained in **Section 4.4.3.2**. If propylene glycol monomethyl ether acetate is present, use the alternate column (**2.2.2**) for quantifying the parachlorobenzotrifluoride in the sample (**NOTE 4**).

NOTE 4: If the alternate column (**2.2.2**) is preferred, use only one half of the weights required for the sample, standard and internal standard.

4.4.4 Determination of Response Factor (R_{PCBTF}) for Parachlorobenzotrifluoride.

4.4.4.1 Inject 1 μ l of the solvent into the gas chromatograph to check for contamination. If contaminated, open a fresh bottle and repeat the step.

4.4.4.2 Weigh accurately 0.2 g (± 0.0001 g) of the parachlorobenzotrifluoride and 0.2 g of ethanol (± 0.0001 g) in a pre-weighed sample vial containing 4 ml of DMF. Cap and shake the vial contents thoroughly for 15 minutes, using the Burrell Wrist Action Shaker. The mixture may be injected into the gas chromatograph immediately after shaking.

4.4.4.3 Using a 10 μ l syringe, inject separately 1 μ l of the mixture from (**4.4.4.2**) into the gas chromatograph. Integrate and record the peak areas of ethanol and the para-chlorobenzotrifluoride. Retain the chromatogram. The order of elution is ethanol, DMF and parachlorobenzotrifluoride.

4.5 Calculation for the Response Factor, R_{PCBTF} , of Parachlorobenzotrifluoride.

- 4.5.1** The response factor, R_{PCBTF} is determined by means of the following equation:
(NOTE: 5)

$$6.6.1.1 \quad R_{PCBTF} = \frac{W_i \times A_{PCBTF}}{W_{PCBTF} \times A_i}$$

Where: W_i = The weight of the internal standard.
 W_{PCBTF} = The weight of parachlorobenzotrifluoride.
 A_{PCBTF} = The peak area of parachlorobenzotrifluoride.
 A_i = The peak area of the internal standard

NOTE 5: It is necessary to determine the response factor for parachlorobenzotrifluoride with each series of determinations.

4.6 Gas Chromatographic Determination of the Parachlorobenzotrifluoride Content of the Coating.

- 6.6.1** Weigh accurately 0.4 to 0.6 g (**± 0.0001 g**) of the mixed coating (**4.1.1**) and 0.2 g (**± 0.0001 g**) of ethanol in a tared vial containing 4 ml of DMF. Immediately cap the vial (**NOTE 6**).

NOTE 6: If the amount of PCBTF in the sample is more than 60% by weight, rerun the analysis using a smaller sample weight (0.2 to 0.4 grams).

- 4.6.2** Shake the mixture on a Burrell Wrist Action Shaker for 15 minutes. It is essential that the sample be thoroughly mixed. Allow the sample to stand undisturbed for about 5 minutes prior to injection. This is to allow the solids to settle at the bottom of the vial.
- 4.6.3** Inject a 1 µl aliquot of the supernatant liquid from (**4.6.2**) into the gas chromatograph. The area of the parachlorobenzotrifluoride and the ethanol peaks are integrated and recorded. Retain the chromatogram (**See Figures I and II**).
- 4.6.4** It is a good practice to confirm the presence and concentration of the parachlorobenzotrifluoride, using the alternate column (**2.2.2**).

4.7 Calculation for % Parachlorobenzotrifluoride in the Coating.

4.7.1 Using the data obtained in **(4.6.3)**, calculate the weight % of parachlorobenzotrifluoride in the sample, as follows:

$$\mathbf{4.7.1.1} \quad \% \text{ PCBTF (W/W)} = \frac{A_{\text{PCBTF}} \times W_i}{A_i \times W_s \times R_{\text{PCBTF}}} \times 100$$

Where:

- A_{PCBTF} = Area of the PCBTF peak
- A_i = Area of the internal standard peak.
- W_i = Weight of the internal standard.
- W_s = Weight of the coating.
- R_{PCBTF} = Response factor for PCBTF.

4.8 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than $\pm 1\%$ (absolute) of the mean.

5) CALCULATION FOR COMPLIANCE OF COATING CONTAINING PARACHLOROBENZOTRIFLUORIDE

$$\mathbf{5.1} \quad \text{Weight of Total Volatile (g/l Coating)} = 1000 \text{ ml/l} \times (4.3.6) \times (4.2.4) \times 10^{-2}$$

Where: (4.3.6) = Density of Coating (g/ml)
(4.2.4) = % Total Volatiles in the Coating (W/W)

$$\mathbf{5.2} \quad \text{Weight of PCBTF (g/l Coating) of PCBTF} = 1000 \text{ ml/l} \times (4.3.6) \times (4.7.1.1) \times 10^{-2}$$

Where: (4.7.1.1) = % PCBTF (W/W)

$$\mathbf{6.6} \quad \text{Volume (ml) of PCBTF (ml/l Coating)} = \frac{(5.2)}{D_{\text{PCBTF}}}$$

Where: $D_{\text{PCBTF}} = 1.353 \text{ g/ml}$

$$\mathbf{5.4} \quad \text{Grams VOC/l Coating (less PCBTF)} = \frac{[(5.1) - (5.2)] \times 1000 \text{ ml/l}}{[1000 \text{ ml/l} - (5.3)]}$$

$$\mathbf{5.5} \quad \text{lb VOC/gal coating (less PCBTF)} = (5.4) \times 8.34 \times 10^{-3}$$

Where: $8.34 \times 10^{-3} = \frac{3.785 \text{ l/gal}}{454 \text{ g/lb}}$

5.6 For low solids materials, where PCBTF is considered part of the coating:

5.6.1 Grams VOC/l Coating = [(5.1) - (5.2)]

5.6.2 lb VOC/gal Coating = (5.6.1) x 8.34 x 10⁻³

6) REFERENCES

- 6.1** Hollis, O.L., "**Separation of Gaseous Mixtures using Porous Aromatic Polymer Beads**", Anal, Chem. 38, 309, 1966.
- 6.2** "**Volatile Content of Paint**", ASTM Designation D2369-95, Book of ASTM Standards.
- 6.3** "**Density of Paint, Varnish, Lacquer and Related Products**", ASTM Designation D1475-90, Book of ASTM Standards, Vol 6.01, 1990.
- 6.4** "**Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatography**", ASTM Method D3792-91, Book of ASTM Standards
- 6.5** "**Determination of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatography**", ASTM Method D4457-85 (1991), Book of ASTM Standards.
- 6.6** "**BAAQMD Manual of Procedures**," Vol.3, Method 22.

Analytical Column: 12' x 1/8" O.D. SS Column packed with
20% SP2100/0.1% Carbowax 1500 on 100/120
mesh Supelcoport

GC parameters:

	<u>Initial</u>	<u>Final</u>
Oven Temperature (°C)	60	200
Time Delay (Min)	5	10
Temperature Program Rate (°C/min)	5	
*Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He	
Carrier Gas Flow (cc/min)	20	
Injection Sample Size (µl)	1	

*Glass Sleeve insert is used in the injection port.

C-R4A CHROMATOPAC CH-2 REPORT No.=55 CHROMATOGRAM=2:LA9/12.C12 00/00/06 03:44:05

Analysis File : 2:SP21CA.R15

SHIMADZU GC -14-A FID
SP2100 CARBOWAX 1500

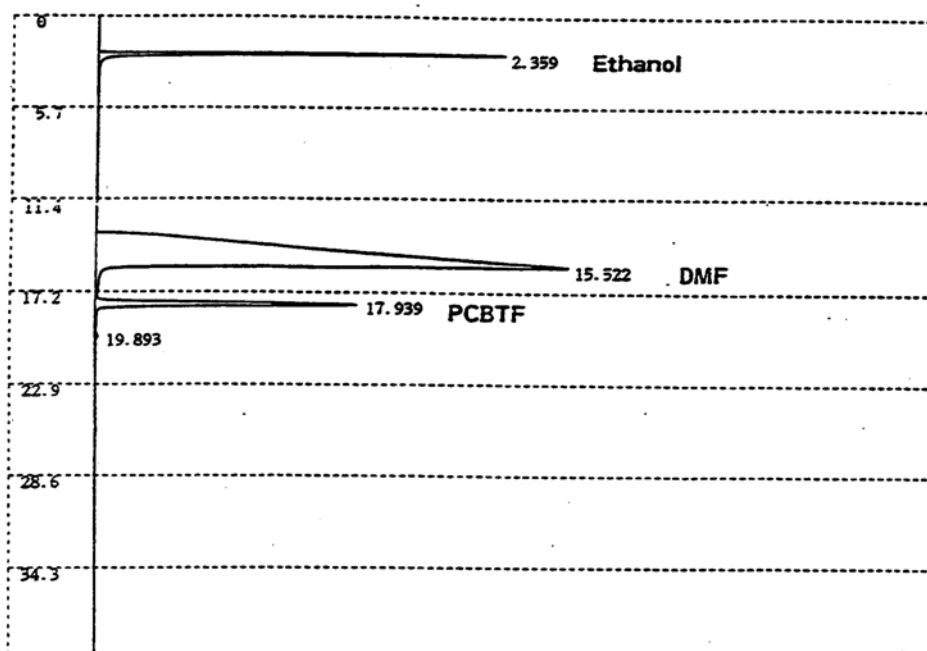


FIGURE I

A Typical Chromatogram
Using the Primary Column (2.2.1)

Analytical Column: 60M x 0.53mm I.D. DB-Wax Column

GC parameters:

	Initial	Final
Oven Temperature (°C)	70	200
Time Delay (Min)	13	10
Temperature Program Rate (°C/min)	30	
*Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He	
Carrier Gas Linear Velocity (cm/sec)	85	
Injection Sample Size (µl)	1	

*Glass Sleeve insert is used in the injection port.

C-R4A CHROMATOPAC CH=1 REPORT No.=25 CHROMATOGRAM=2:1C10/3.C24 95/11/03 09:03:38

Analysis File : 1:0FILE1

GC-14A-2
60M X 0.53MM DB-WAX 1 MICRON FILM THICKNESS
FID

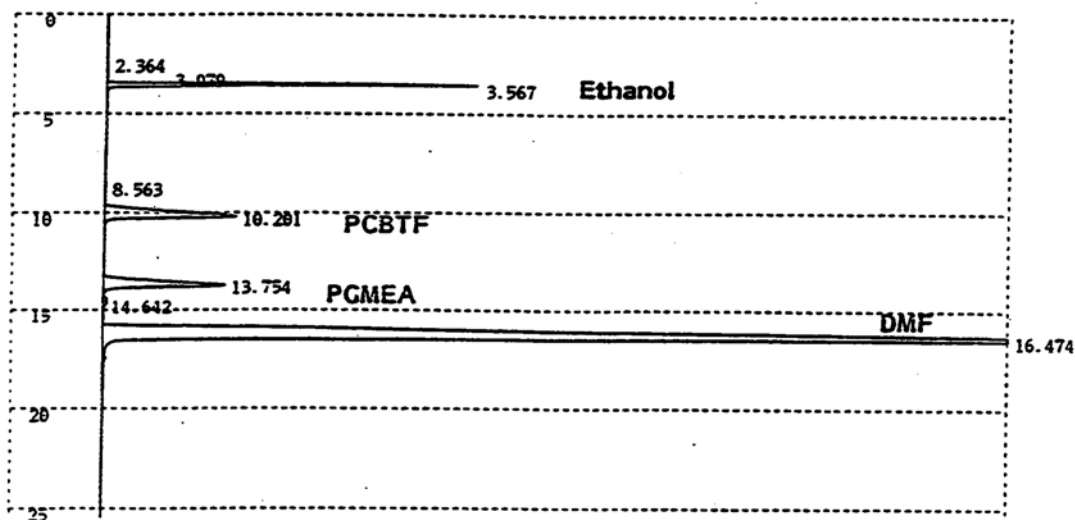


FIGURE II

A Typical Chromatogram
Using the Alternate Column (2.2.2)